Propane Dehydrogenation with Better Stability by a Modified Pt-Based Catalyst

N. Hataivichian, K. Suriye, S. Kunjara Na Ayudhya, P. Praserthdam, S. Phatanasri

Abstract—The effect of transition metal doping on Pt/Al_2O_3 catalyst used in propane dehydrogenation reaction at 500˚C was studied. The preparation methods investigated were sequential impregnation (Pt followed by the 2nd metal or the 2nd metal followed by Pt) and co-impregnation. The metal contents of these catalysts were fixed as the weight ratio of Pt per the 2nd metal of around 0.075. These catalysts were characterized by N_2-physisorption, TPR, CO-chemisorption and NH_3-TPD. It was found that the impregnated 2nd metal had an effect upon reducibility of Pt due to its interaction with transition metal-containing structure. This was in agreement with the CO-chemisorption result that the presence of Pt metal, which is a result from Pt species reduction, was decreased. The total acidity of bimetallic catalysts is decreased but the strong acidity is slightly increased. It was found that the stability of bimetallic catalysts prepared by co-impregnation and sequential impregnation where the 2nd metal was impregnated before Pt were better than that of monometallic catalyst (undoped Pt one) due to the forming of Pt sites located on the transition metal-oxide modified surface. Among all preparation methods, the sequential impregnation method- having Pt impregnated before the 2nd metal gave the worst stability because this catalyst lacked the modified Pt sites and some fraction of Pt sites was covered by the 2nd metal.

Keywords—Alumina, dehydrogenation, platinum, transition metal.

I. INTRODUCTION

PROPYLENE is an important chemical intermediate. It can be used to produce polymers, mainly in polypropylene, acrylonitrile, propylene oxide and etc. Propylene is mainly produced by steam cracking and fluid catalytic cracking (FCC), where propylene is produced as a by-product, and thus the propylene yield is not always good. On the other hand, the demand of propylene in industry is increasing. Propylene sales are supposed more than 90 billion$ in 2012. Therefore, propylene production has a great interest in commercial [1]. The catalytic dehydrogenation of propane to produce propylene is also possible in an industry. However, this reaction suffer from the quickly deactivated of catalyst, due to coke deposition. As a result, improving the catalytic stability of propane dehydrogenation is a very interested research.

Since 1980s to 1990s, the Pt and transition metal catalysts

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had been studied in order to find a suitable promoter for Pt supported on alumina catalysts for various reactions, such as reforming, hydrodechlorination or hydroconversion [2]-[7]. P. Kanta Rao et al. [7] and Jose L. Contreras et al. [8] found that the addition of transition metal to Pt/Al_2O_3 can help promote the stability of catalyst in hydrodechlorination of chlorobenzene and benzene hydrogenation reactions, respectively.

Nevertheless, the propane dehydrogenation reaction by Pt-based catalyst modified with transition metal has not yet been studied. Therefore, this study aims to investigate the catalytic performance of transition metal doping on Pt/Al_2O_3 catalysts in propane dehydrogenation reaction. Moreover, the effect of preparation methods of bimetallic catalysts was also studied.

II. EXPERIMENTAL

A. Catalyst Preparation

The γ-Al_2O_3 was used as a support (Sasol Germany GmbH, Germany). It was crushed and sieved into mesh size 40/60 before being used. The bimetallic catalysts were prepared by co-impregnation and sequential impregnation methods, using chloroplatic acid hydrate (Sigma-Aldrich chemistry, UK, 38% Pt basis) and the ammonium hydrate of transition metal (Sigma-Aldrich chemistry, USA, 99.99% trace metal basis) as precursors. The metal contents were fixed as the weight ratio of Pt per the 2nd metal of around 0.075. The impregnated mixture was dried overnight at 110°C and calcined at 500°C in air. The co-impregnation catalyst was designated as $(PtX)/Al_2O_3$, and the sequential impregnation catalysts were designed as X-Pt/Al_2O_3 and Pt-X/Al_2O_3 for platinum followed by the 2nd metal and the 2nd metal followed by platinum catalysts, respectively. Moreover, the Pt/Al_2O_3 was also prepared for use as a reference catalyst.

B. Catalyst Characterization

N_2-physisorption was performed by BET-method on a Tristar (Micronmeritics) instrument. Measurements were performed with nitrogen as adsorbate at -196°C, after pretreatment of the samples at 200°C under nitrogen flow for 12 hours.

The H_2-TPR was performed to investigate the reducibility of catalysts by a Micromeritic Chemisorb 2750 automated system. The sample was pretreated under N_2 flow at 500°C for 1 h to remove a moisture, then being cooled down to temperature at 50°C. Subsequently, the TPR profiles were recorded under the 10% H_2/Ar flow from 50 to 750°C with a heating rate of 10°C/min. The amount of hydrogen uptake was determined by measuring the areas of the reduction profiles on

the thermal conductivity detector (TCD).

CO-Pulse Chemisorptions of catalysts were performed in a Micromeritic ChemiSorb 2750 automated system equipped with the thermal conductivity detector (TCD). Platinum dispersion is determined by pulsing carbon monoxide over the reduced catalyst. Samples were placed in a quartz tube, incorporated and prior to chemisorptions; the catalyst was reduced in a flow of hydrogen (25 cc/min) at 550°C for 2 h. Then, the sample was purged with helium and cooled down to room temperature. Carbon monoxide is pulsed at room temperature over the reduced catalyst until the TCD signal is constant.

The NH₃-TPD process was monitored by a Micromeritic Chemisorb 2750 automated system. Samples were placed in a quartz tube and pretreated at 500°C in a flow of helium which was maintained for 1 h to remove a moisture. The sample was saturated with 15% NH₃/He at 100°C. After saturation, the physisorbed ammonia was desorbed in a helium gas flow for about 1.0 h. Then, the sample was heated from saturation temperature to 500°C at a heating rate of 10°C/min. The amount of ammonia effluent was detected on the thermal conductivity detector (TCD).

C. Catalytic Test

The catalytic performance of catalysts was measured in a stainless steel tubular reactor with inner diameter (ID) of 3/4 inch to which a type K thermocouple was mounted. Prior to the reaction, the catalyst was reduced at 550°C under hydrogen gas flow for 2 h, then purged with nitrogen gas for 20 minutes and cooled down to reaction temperature of 500°C and pressure of 1 bar. Next, propane (>99.5% purity) was fed to the reactor using weight hourly space velocity (WHSV) of 0.16 h⁻¹. The sampling was made at 6 hours on stream, and sample analysis was performed on an Agilent 7820A gas chromatograph equipped with a column of packed HP-PLOT Al₂O₃ "M" deactivated (50 m with 8 μm ID) and a flame ionization detector (FID).

III. RESULTS AND DISCUSSION

A. Textural Properties

The textural properties of catalysts are listed in Table I. The specific surface area was calculated using BET method. From the results, it can be seen that the BET surface area of all catalysts showed no significant change. This observation agrees with G.A. Fuentes et al. [3], [8]. This result indicates that the addition of the transition metal was highly dispersed on the alumina support and almost did not affect the surface area of catalysts irrespective of the preparation methods.

TABLE I
SUMMARY OF SURFACE AREAS OF CATALYSTS

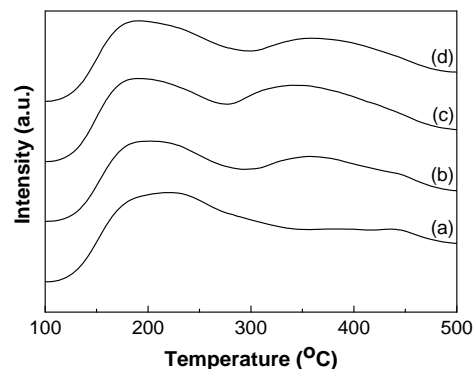| Catalysts	$S_{BET}(m^2/g)$
Pt/Al₂O₃	192.58
X-Pt/Al₂O₃	191.54
Pt-X/Al₂O₃	194.43
(PtX)/Al₂O₃	193.07

S_{BET} : BET surface area

Fig. 1 NH₃-TPD profiles of catalysts; (a) Pt/Al₂O₃, (b) X-Pt/Al₂O₃, (c) Pt-X/Al₂O₃ and (d) (PtX)/Al₂O₃

TABLE II
ACIDITY OF CATALYSTS

Catalysts	Acidity (μmol NH₃/g.cat)		
	Total acid	Weak acid	Strong acid
Pt/Al₂O₃	290.99	121.00	169.99
X-Pt/Al₂O₃	256.19	80.81	175.37
Pt-X/Al₂O₃	281.91	72.19	209.72
(PtX)/Al₂O₃	257.13	90.16	166.97

Value of acidity obtained by deconvolution of NH₃-TPD profiles in Fig. 1.
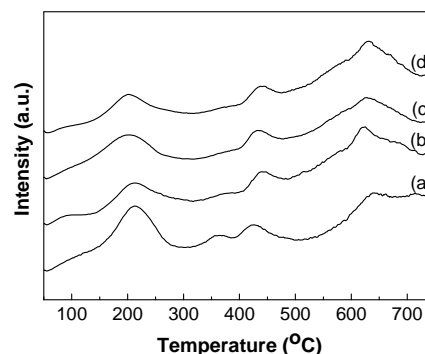

Fig. 2 TPR profiles of catalysts; (a) Pt/Al₂O₃, (b) X-Pt/Al₂O₃, (c) Pt-X/Al₂O₃ and (d) (PtX)/Al₂O₃

B. Temperature Programmed Desorption of Ammonia

The NH₃-TPD was used to measure the amount and strength of acidity of catalysts. Fig. 1 shows the NH₃-TPD profiles of all catalysts in the temperature range of 100 to 500°C. All catalysts showed two desorption peaks corresponding to weak and strong acid sites [9]. Table II shows the value of total acid, weak acid and strong acid separated by deconvolution of the NH₃-TPD profiles. It can be seen that the total acidities of bimetallic catalysts were lower than that of Pt/Al₂O₃ catalyst as follows: Pt/Al₂O₃ > Pt-X/Al₂O₃>(PtX)/Al₂O₃ and X-Pt/Al₂O₃. In view of weak acidity of bimetallic catalysts, it apparently decreased. Ahmed K. Abou-Gheti et al. [2] assumed that the transition metal adsorbed selectively on the acid site of alumina, and masked these sites. Thus, the weak acidity of our results was decreased. However, the strong acidities of Pt-X/Al₂O₃ and X-Pt/Al₂O₃ were increased and that of (PtX)/Al₂O₃ was not significantly decreased. This results show that the acidity of

the transition metal-oxide itself affected the increase of strong acid site.

C. Temperature Programmed Reduction

The effect of the transition metal addition on the reduction property of the bimetallic catalysts in the temperature range of 50 to 750°C is shown in Fig. 2. All catalysts had a large reduction peak centered around 640°C, associated to the reductive dehydroxylation of alumina support [10]. The monometallic Pt/Al_2O_3 catalyst showed the low temperature reduction peak centered at 216°C with a small shoulder at 120°C, which was assigned to the reduction of platinum species in the weak interaction with alumina [11]. The next peak located at 365°C was assigned to the reduction of platinum species in the strong interaction with alumina [12]. The other peak at 425°C can be attributed to the reduction of oxychlorinated platinum species [13]-[15]. For the bimetallic platinum and transition metal catalysts, [3] found that a very stable subsurface transition metal-alumina structure may have been formed, so they did not found any reduction band of this metal until 1000°C. From the results, the reduction peaks of platinum in weak interaction with alumina of bimetallic catalysts were smaller and shifted to the lower temperature when compared with the Pt/Al_2O_3 catalyst. Moreover, the reduction peaks of platinum in strong interaction with alumina were almost disappeared and the reduction peaks of oxychlorinated platinum were shifted to higher temperature. These phenomena were explained by the interaction of platinum with the transition metal species. Platinum ions were kept from reducing by their interaction with the transition metal containing structures [8] and this metal did affect the surface structure in the neighborhood of the platinum atoms [3]. These effects caused the bimetallic catalysts contained less active platinum metal than the Pt/Al_2O_3 catalyst [7].

D. CO Chemisorption

Table III shows the amount of CO adsorbed and Pt dispersion of Pt/Al_2O_3 and bimetallic catalysts. The monometallic Pt/Al_2O_3 catalyst showed the highest Pt dispersion, while Pt dispersion of the bimetallic catalysts decreased about 40%. This result agrees with [3], [8]; they founded that the amount of H_2 chemisorption has decreased in the bimetallic catalysts, especially up to 70% from the monometallic Pt catalyst in case of the addition of Pt to XO_3/Al_2O_3. This observation was a consequence from the interaction of platinum and the transition metal causing the fraction of unreduced platinum as described in the result of TPR. Moreover, $X-Pt/Al_2O_3$ showed the lowest Pt dispersion and $Pt-X/Al_2O_3$ had the highest among the bimetallic catalysts. This result may be due to the effect of impregnating sequence. When platinum was impregnated first and followed by the transition metal, some fraction of platinum species was covered by the transition metal and unable to reduce. Conversely, when the transition metal was impregnated before platinum, none of platinum that was covered by the transition metal, thus this catalyst had more reduced platinum and Pt dispersion.

TABLE III
CO CHEMISORPTION OF CATALYSTS

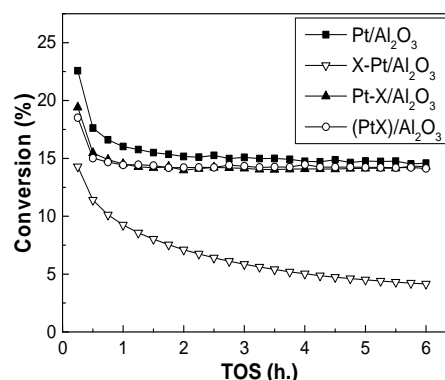| Catalysts	Amount of CO adsorbed (μmol CO/g.cat)	Pt dispersion (%)
Pt/Al_2O_3	20.67	1.34
$X-Pt/Al_2O_3$	11.30	0.73
$Pt-X/Al_2O_3$	12.32	0.80
$(PtX)/Al_2O_3$	11.89	0.77

Fig. 3 Propane conversion with time on stream

E. Propane Dehydrogenation Reaction

The conversion with time on stream of all catalysts in reaction of propane dehydrogenation is shown in Fig. 3. The Pt/Al_2O_3 catalyst exhibited a 22.57% initial conversion. After 6 h on-stream, propane conversion decreased to 14.59%. When the transition metal was added, the platinum active sites were decreased, thus the lower initial conversion was observed (14.28%, 19.41% and 18.52% for $X-Pt/Al_2O_3$, $Pt-X/Al_2O_3$ and $(PtX)/Al_2O_3$, respectively). However, the final conversion at 6 h on-stream of $Pt-X/Al_2O_3$ and $(PtX)/Al_2O_3$ came near with that of the Pt/Al_2O_3 catalyst. Therefore, these two bimetallic catalysts were less deactivated and reached the steady state faster than the monometallic catalyst. In the case of $X-Pt/Al_2O_3$, the lowest initial and final conversions were observed according to the lowest Pt dispersion as well as the highest deactivation rate.

This observation may be explained by the two types of active platinum sites [16]. A first platinum type locates directly on the carrier surface defined as Pt_1 sites, which are responsible for the hydrogenolysis and coking reactions. While another type of platinum locates on the metal-oxide modified carrier surface defined as Pt_2 sites. These active sites are beneficial to the dehydrogenation reaction. Moreover, the transition metal-oxide on the surface can also modify the electronic properties of the platinum [17]; this effect can decrease the likelihood of pathways leading to the formation of deactivating species.

The above explanation indicated that the $X-Pt/Al_2O_3$ catalyst lacked the Pt_2 sites and some fraction of Pt_1 sites was covered by the transition metal, leading to the lowest conversion and the highest deactivation. On the other hand, the $Pt-X/Al_2O_3$ and $(PtX)/Al_2O_3$ catalysts can form the Pt_2 sites, resulting in the better stability than the Pt/Al_2O_3 catalyst.
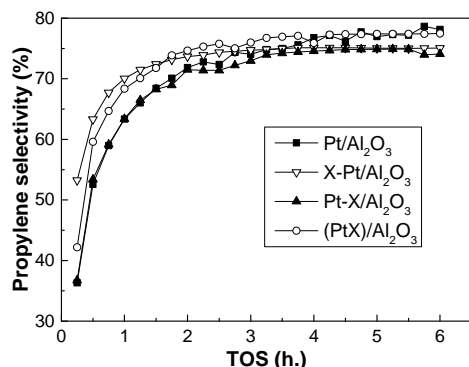
Fig. 4 Propylene selectivity with time on stream

The selectivity of propylene with time on stream of all catalysts is shown in Fig. 4. The propylene selectivity of each different catalyst was enhanced with time on stream and reached the similar steady state value. This behavior can be explained by the catalysts having a density of hydrogenolysis and cracking sites, which produce other hydrocarbon products. These sites were quickly poisoned by coke, with the subsequent deactivation, as a result of decreasing the side reactions [18].

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